

Kinetics, Thermodynamic, and Isotherm Modeling for Biosorption of Heavy Metals from Aqueous Environment onto Lignocellulosic Biomass

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ABSTRACT: The present study evaluates the performance of the lignocellulosic fibers *Momordica Charantia* for the sequestration of lead (II), zinc (II), chromium (VI), and copper (II) ions from aliquid medium. The biomass has been analyzed and depicted by Fourier-transform infrared spectroscopy and scanning electron microscope. The biosorption rate of these toxic metals depended on contact time and pH solution. The maximum biosorption rate was found at pH = 6.0 for the biosorption of divalent metals and for hexavalent chromium the maximum rate was obtained at pH = 2.0. At optimal conditions, the experiment results elucidate that metals uptakes are rapid systems at 60 min equilibrium time, and the order of uptake metal ions is lead > Chromium > Zinc > Copper. The adsorption isotherms were studied and modeled using Langmuir, Freundlich, and Temkin equations. The Langmuir isotherm model presents goodness fit for all metals studied by height coefficient of coloration, with a maximum capacity of 8.9, 5.9, 4.67, and 3.9 mg/g for lead (II), chromium (VI), Zinc (II), and Copper (II), respectively. Kinetic modeling elucidates that the biosorption processes followed better the pseudo-second-order model. Furthermore, the thermodynamic factors demonstrated that the biosorption behavior of heavy metals was favorable, spontaneous, and exothermic processes. Finally, this study showed that the *M. Charantia* threads could be considered an excellent biomaterial to be employed as an effective sorbent for removing heavy metals in the liquid environment.

KEYWORDS: Biosorption, heavy metals; Lignocellulosic fibers; Sequestration, Kinetics modeling; Adsorption isotherms.

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INTRODUCTION

In recent times, considerable attention has been paid to manage environmental pollution generated by hazardous materials such as toxic metals. Industries such as the metal plating industry, tanneries, paper and pulp industries, metallurgy and mining industry, energy and fuel production, glass production industry and fertilizer industry, are some of the primary heavy metals contaminated effluent producing industries [1]. Due to the activities like surface finishing, production of chemicals, milling, and mining, a large amount of effluent is generated that is regularly discharged into the water bodies [2]. Due to toxic, non-degradable, mutagenic, and carcinogenic nature of heavy metals, it becomes vital to treat them properly before discharging into the ecosystem. Effluent mainly consists of pharmaceutical compounds, dyes, and heavy metals. These contaminants need to be appropriately addressed as they can stay in the environment for infinite time and, in turn, become a formidable threat to the ecosystem. Arsenic Cadmium, Chromium, Nickel, Lead, Zinc, Mercury, Copper, etc. are some of the metals that are commonly found in industrial effluents. These metals tend to form complexes with biological matter comprising oxygen, sulfur, and nitrogen and hence if absorbed by living beings, it can result in modifying the molecular framework of nucleic acids, and protein, or inhibiting the activity of enzymes, ultimately leading to carcinogenic or toxicological effects [1].

Many techniques have been developed to sequester poisonous metals from the liquid phase, such as evaporation, membrane processes, precipitation, electro-coagulation, etc. However, these conventional processes have several disadvantages, such as unsalable heavy metal ion sequestration, generation of toxic sludge, and high reagent requirement [3,4]. There is an urgent need to develop more cost-effective methods due to the high costs of traditional methods used to remove heavy metals from wastewaters. Biosorption is an alternative process that employs a biotechnology innovation and cost-adequate support for sequestering heavy metals from an aqueous medium. In the biosorption process, biomasses are engaged, which complex heavy metal ions *via* the functioning of active sites or legends located on the macromolecular of the biomaterial [5, 6]. Among the biological materials that can attract toxic metal ions, we mention the lignocellulosic fibers, algae, microorganisms, and yeast [7].

The main components of the lignocellulosic fibers refer to plant material composed of cellulose are cellulose, hemicelluloses, and lignin. Cellulose is a principal constituent, and its percentage plays a vital parameter in describing the properties of the fiber. The crystalline index of the lignocellulosic threads has a crucial influence on the mechanical characteristic of the thread [8, 5].

The present research examines a new lignocellulosic biosorbent, *Momordica Charantia*, and its feasibility for heavy metal sequestration from an aqueous medium. It is low-cost and readily available in several regions of Algeria. *Momordica Charantia* comprises of 61 % cellulose, 29 % hemicelluloses, and 10 % lignin and is classified as lignocellulosic material [8]. Batch experiments carry out the biosorption of heavy metals onto this biomaterial fiber. Biosorption optimization is investigated. Moreover, the isotherm and kinetic study are evaluated, and the thermodynamic parameters are determined. Results from this research can be applied to affirm the applicability of *Momordica Charantia* for toxic metals scavenging from industrial wastewater.

EXPERIMENTAL SECTION

Adsorbate

The chemical agents employed in this paper were of analytical grade reagents in chemistry. Concentrated solutions (1000ml) of lead (II), zinc (II), Copper (II), and Chromium (VI) ions were prepared by solubilizing a determined portion of their nitric salt in diluted heavy metal concentrations from the concentrated solution. Each solution was diluted to the aqueous feed initial metal concentration for each experiment. The pH of each solution was equilibrated by adding drops of diluted solutions to 0.1M Hydrochloric acid or Sodium hydroxide before commencing the biosorption experiments. The concentration of lead (II), zinc (II), chromium (VI), and copper (II) ions after biosorption was detected using atomic absorption spectrophotometer (AASUNICAM-969-JAPON). In the case of hexavalent chromium, the concentrations were carried out based on the standard colorimetric technique. A sample of (1) of the chromium solution is taken and mixed in an acid solution with a complexing agent, 1, 5-diphenylcarbazide. For this reason, a purple-violet complex appears after ten minutes, and its intensity is calculated UV visible spectroscopy (IR-V-700 JASCO- FRANCE) at 540 nm [9].

Biosorbent

As a kind of a tremendous biological support, Algerian *Momordica Charantia* biomaterials can be employed as bio-adsorbent for the scavenging of lead (II), zinc (II), chromium (VI), and copper (II) ions. For this reason, the *Momordica Charantia* threads were washed with be-distilled water to eliminate salts, lime-scale, and sediment from the sorbent. After that, they were dried at room temperature for 24 then in an oven at 50 ° C for 48 h. The *Momordica Charantia* were then finely ground, washed again with be-distilled water, and then replaced in the oven at 90 ° C. for 24 hours.

Batch experiment

The biosorption experiment was employed by mixing a portion of biosorbent with 100 of metal solution in 250 at a 120 rpm/min speed. The biosorbent was isolated from the metal solution by centrifugation at 5000 rpm for 10 min. Once the biosorbent is introduced in a metal solution, biosorption of metal ion on *Momordica Charantia* will take place. The heavy metal ion in solution will decrease until a certain value (equilibrium value) is reached. The time needed for the process is the equilibrium time. The effect of pH on the equilibrium time for biosorption of lead (II), zinc (II), chromium (VI), and copper (II) ions was studied using pH values of 1.0, 2.0, 3.0, 4.0, 5.5, 6.0, 7.0 and 8.0. These values were measured before and after tests, and no significant change in pH values was observed. After preparation of a metal solution with an initial concentration of approximately 10 mg/L with a pH that was adjusted using with 0.5M acid nitric or 0.5 M sodium hydroxide solution, a certain amount ((1-4 g/100) of *Momordica Charantia* without handling was added. In the meantime, a control without *Momordica Charantia* was set up, while pH in the reaction mixture was not controlled. Samples were tested at 5, 15, 30, 50, 80, 120, 150, and 180 min and analyzed for residual metal ion concentration. Each experiment was performed in triplicate and the amount of biosorption at time t, qt (mg/g), was calculated using the following formula [2, 11]:

$$q_e = \frac{(C_0 - C_e)}{M_B} \times V_S \quad (1)$$

Where q_e is the metal uptake capacity (mg/g), C_0 is the initial metal concentrations (ppm), C_e final metal concentration (ppm), V_S is the volume of each metal

solution (L), and M_B is the mass of *Momordica Charantia* (g). Biosorption rate was computed from the following formula:

$$R(\%) = \frac{(C_0 - C_e) \times 100}{C_0} \quad (2)$$

To obtain information on the active sites present on the macromolecular of *Momordica Charantia*, Fourier Transform InfraRed spectroscopy (IR Prestige-21, Shimadzu, Japan) was employed. A portion of 0.1 g of MC was encapsulated in 1 g of KBr, and FT-IR spectra were determined with (IR Prs-21, Shimadzu spectrometer). The FT-IR spectrum was obtained on average of 400–4000 cm^{-1} . In Addition, the structure of *Momordica Charantia* (MC) was depicted by scanning electron microscopy (HT S2600 N-JAPON).

Desorption study

Momordica Charantia (1.0 g) was mixed with 100 of each metal ion (lead, zinc, chromium, and copper) to study the regeneration and desorption phenomenon. After equilibration for 90 min at 25°C, the *Momordica Charantia* was recovered, and the biosorption capacity (mg/g) was determined. Furthermore, Five desorbing solutions, such as: 0.1 M Sodium hydroxide, 0.1 M Hydrochloric acid, 0.1 M Sulfuric acid, tap water, and de-ionized water, were applied to desorbed lead, zinc, chromium, and copper ions accumulated on the *Momordica Charantia*.

Percentage desorption was determined using the formula below [2]:

$$\text{Percentage desorption} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Biosorbent characterization (FT-IR and SEM)

The quality and quantity of sorption/chemisorption or physisorption of metals onto the biomass surface is strongly determined by functional groups present on the plant material [12]. Therefore, FT-IR characterisation was carried out to analyze the major functional groups which exist in the biosorbent. For the comparative research, the data of native and loaded MC with heavy metal ions (lead (II), Zinc (II), and Copper (II), and Chromium (VI) ions) were analyzed. The appended FT-IR spectrums are present in Fig.1 (A, B, C, D, and E). In all the data, a broadband range of 3200-3550 cm^{-1}

indicates the existence of hydroxyl groups associated with the N–H pick of amino groups [11]. The difference in pick intensity is identical to the difference in the concentration of specific functional groups attributed to the picks. The existence of broadband justified it in the frequency bandwidth of 3200- 3550 cm^{-1} due to the presence of the hydroxyl group [9]. Two squeaky bands at 2925 and 2852 cm^{-1} correspond to the -CH asymmetric and symmetric stretching vibrations of methylene hydrogen [11]. Each spectrum demonstrates a quick, intense peak at 1752 cm^{-1} ascribed to the aromatic groups (C=C, C=O, and conjugated ketones or C=N amide stretching). The methyl asymmetric C-H peaks at 1458, 1053, and 1034 cm^{-1} are attributed to C-O stretching of alcohol or polysaccharides-like substances. Medium intensity broadband in 1050 cm^{-1} is assigned to ν (C-O-C) asymmetrical extension [9, 12]. In comparison to the spectra of loaded MC with heavy metal ions (lead (II), zinc (II), chromium (VI), and copper (II) ions), a slow shift in the peak was remarked (Fig.1 (A, B, D, C, and E)). These changes in the position of the peak occurred because of the linking of lead (II), zinc (II), chromium (VI), and copper (II) ions with amino and hydroxyl groups of *Momordica Charantia*. Thus, the difference in the peak intensity validates the biosorption of lead (II), zinc (II), chromium (VI), and copper (II) ions on the surface of *Momordica Charantia*. The main observable difference among the spectra is; at an intensity of 3000-3800 cm^{-1} representing hydroxyl expansion and the medium intensity peak in the range of 1600-1700 cm^{-1} means carbonyl stretching. These validate the participation of hydroxyl groups in the binding of lead (II), zinc (II), chromium (VI), and copper (II) ions. Slight changes in the frequency of bands confirm the existence of biosorption.

SEM depicts the morphology of the *M. Charantia*. The MC sponge comprises fibril groups disposed of in several directional arrays, forming a natural biometric (Fig. 2a,); the diameter of one fiber is the average (62–123 μm). The structure was depicted at high magnification to observe the internal crude fiber (Fig. 2b). The SEM observation elucidates that the yarn has a heterogeneous surface with an outer lignin stratum on the threads. At high power magnification, the SEM image shows a rougher surface and the presence of several waxy compounds on the native *Momordica Charantia* (Fig. 2c, d).

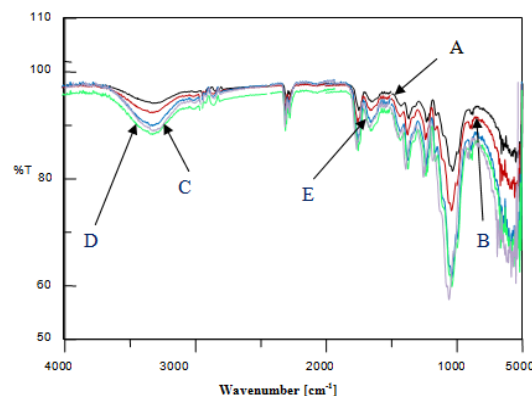


Fig. 1: FT-IR spectrum of *Momordica Charantia* before and after biosorption. A: MC, B: MC-Pb (II), C: MC-Pb-Zn (II), D: MC-Cu (II), E: MC- Cr (VI).

Biosorption optimization

Effect of contact time

The biosorption rate of lead, zinc, chromium, and copper ions with the function of contact time is present in Fig. 3. The efficiency of biosorption concerning contact time on the MC indicates that the removal rate of lead, zinc, chromium, and copper ions was firstly augmented by increasing contact time (min). The bioprocesses are rapid until they attain their maximum uptake; this may maybe due to the several active sites on the *Momordica Charantia*. At these steps, the equilibrium times were reached. After this step, the surface pores of the biosorbent were saturated, and the desorption process started. The slow rate of biosorption at this period could be due to the aggregation of adsorbed metals on the surface of *Momordica Charantia*.

Effect of pH solution

The pH of the solution is an important parameter for controlling the biosorption process. The effect of pH on the biosorption of lead, zinc, chromium, and copper ions was examined. Fig.4 shows these behaviors. Many studies have shown that the pH of aqueous model solutions affects both the solubility of metal ions and the ionization states of biosorbent functional groups [13]. Due to its chemical composition (cellulose, lignin), *Momordica Charantia* biomass has different surface functional groups, such as carboxyl, carbonyl and hydroxyl. These different functional groups show a high affinity towards heavy metals; therefore they can complex the metal ions [14]. Divalent metal cations seemed to be mostly unsorbed at low pH values. Minimal adsorption at high solution

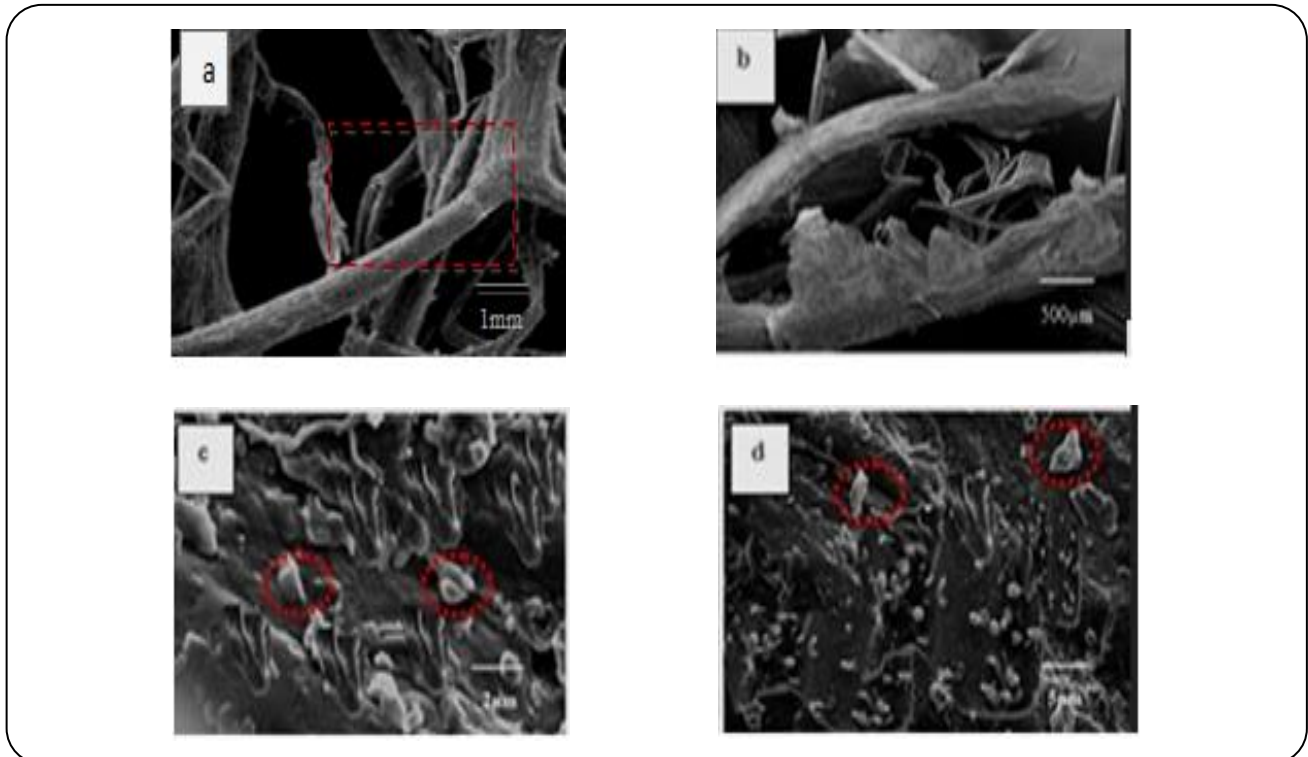


Fig. 2: SEM micrographs of *Momordica Charantia*.

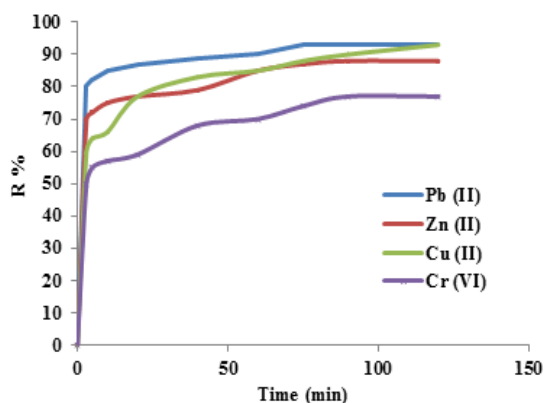
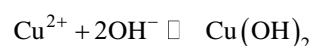


Fig. 3: Effect of contact time onto Biosorption rate.

acidity could be explained by a high concentration and mobility of H^+ ions. That is why, in comparison to lead, copper, and zinc ions, hydrogen ions were adsorbed first on the sorption sites. At lower pH values, the removal was inhibited; this can be due to the competition between hydrogen and lead (II), Zinc (II), and Copper (II) ions on the adsorption sites, with an evident superiority of H_3O^+ , which enclose the oncoming of heavy metal ions as result of the offensive force [1, 17, 18]. At high basic, the sites

in MC would be augmenting the negative charge on the MC Biosorbent, thus facilitating biosorption of lead (II), Zinc (II), and Copper (II) ions with a positive charge on the MC surface [19]. In this research, these compounds at pH =6 would be anticipated to link extra-hardly with the negatively charged linking sites. Based on that, the optimum pH for lead (II), Zinc (II), and Copper (II) ions biosorption were found at pH = 6. The ions are probably bio-adsorbed onto *Momordica Charantia* via ion-exchange process or through hydrogen bonding forming

Lead (II) hydroxide, Lead dioxide, zinc (II) hydroxide, Zinc dihydroxide, and copper (II) hydroxide. The mechanism of binding as previously mentioned as follows:



In the case of Chromium (VI), the results elucidated that the optimum biosorption capacity of Chromium (VI)

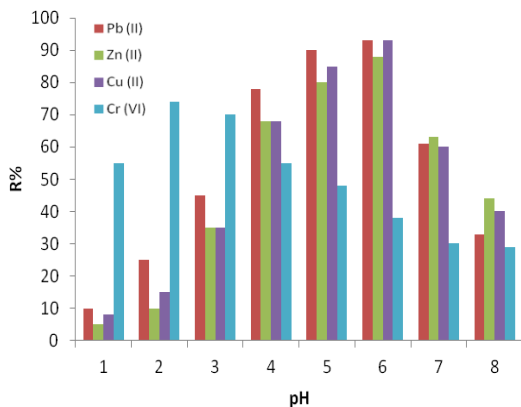


Fig. 4: Effect of pH solution on *Momordica Charantia*.

was obtained at $\text{pH} = 2$. However, the biosorption capacity decreases after this point. This behavior is justified because, at $\text{pH} = 2$, the functional groups on the MC surface undergo a strong hydration, which allows the matrix biomass a positive synoptic charge. Furthermore, the ionic forms of Chromium (VI) that exist in the solution are Hydrogenchromate (HCrO_4^-), Dichromate ($\text{Cr}_2\text{O}_7^{2-}$), trichromate ($\text{Cr}_3\text{O}_{10}^{2-}$), and tetrachromate ($\text{Cr}_4\text{O}_{13}^{2-}$), and this for low pH [8]. Additionally, the biosorption rate recorded reduces with incrementing pH. On the other hand, at higher pH, the solution is concentrated in free hydroxyl radicals which can contend with the anionic molecules of hexavalent chromium on the functional sites available on the surface of *Momordica Charantia* biosorbent.

Effect of-biosorbent content

A significant factor that highly impacts biosorption is the biosorbent content. The biosorption tests were carried out with *Momordica Charantia* contents between 0.1 and 4-g for 100 of metal solution. Fig. 5 illustrates the biosorption capacity effect of *M. Charantia*. It is worth noting that the amount of lead, zinc, chromium, and copper ions adsorbed on MC decreases by increasing the *M. Charantia* content. This could be because the vacant sites have been saturated on the adsorbent surface [20]. The higher MC dosage gave rise to a higher percentage removal of heavy metal ions, providing a significant leading force to defeat all mass transfer resistances of the lead, zinc, chromium, and copper ions between the solute sorbate and *M. Charantia* surface.

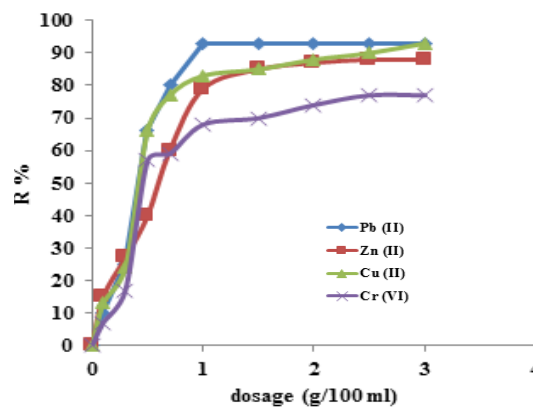


Fig. 5: Effect of *Momordica Charantia* dose.

Biosorption kinetics

Bio-adsorption kinetic explains the steps of the bioprocess. The metal ions can immigrate from the solution to the internal biomaterial in many successive actions, and the amalgamation of several actions can advance the government process. The immigration of sorbate could be both in the mode of mass transfer of the liquid phase neighboring the surface of the biosorbent through the outward space layer covering film, or dispersing of the solute metal into a biosorption [2]. In the bio-adsorption of metals, pseudo-first-order (PFO) and pseudo-second-order models (PSO) were used to explore the plausible rapidity control actions. Non-linear model formulas were employed for bio-adsorption Kinetics of lead (II), Zinc (II), Copper (II), and Chromium (VI) ions are given as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{K_2 q_e^2}{1 + K_2 q_e t} \quad (4)$$

Where q_t and q_e is the biosorption capacity (mg/g) at equilibrium and at time t (min), respectively, and k_1 (1/min) is the rate constant of PFO model K_2 (g/mg/min) is the rate constant of PSO model [2]. For all metals studied, the results indicate that the Pseudo-Second-Order (PSO) are better than the PFS model with high coefficient of determination (Fig. 5 (A, B, C, and D)), indicating the participation of two species in the bioprocess. Based on the documentation, a PSO model best demonstrates heavy metal ions' adsorption [16]. The rate constant of a PSO kinetic model (k_2) decreases with the increment of initial concentration until it attained a peak. These results

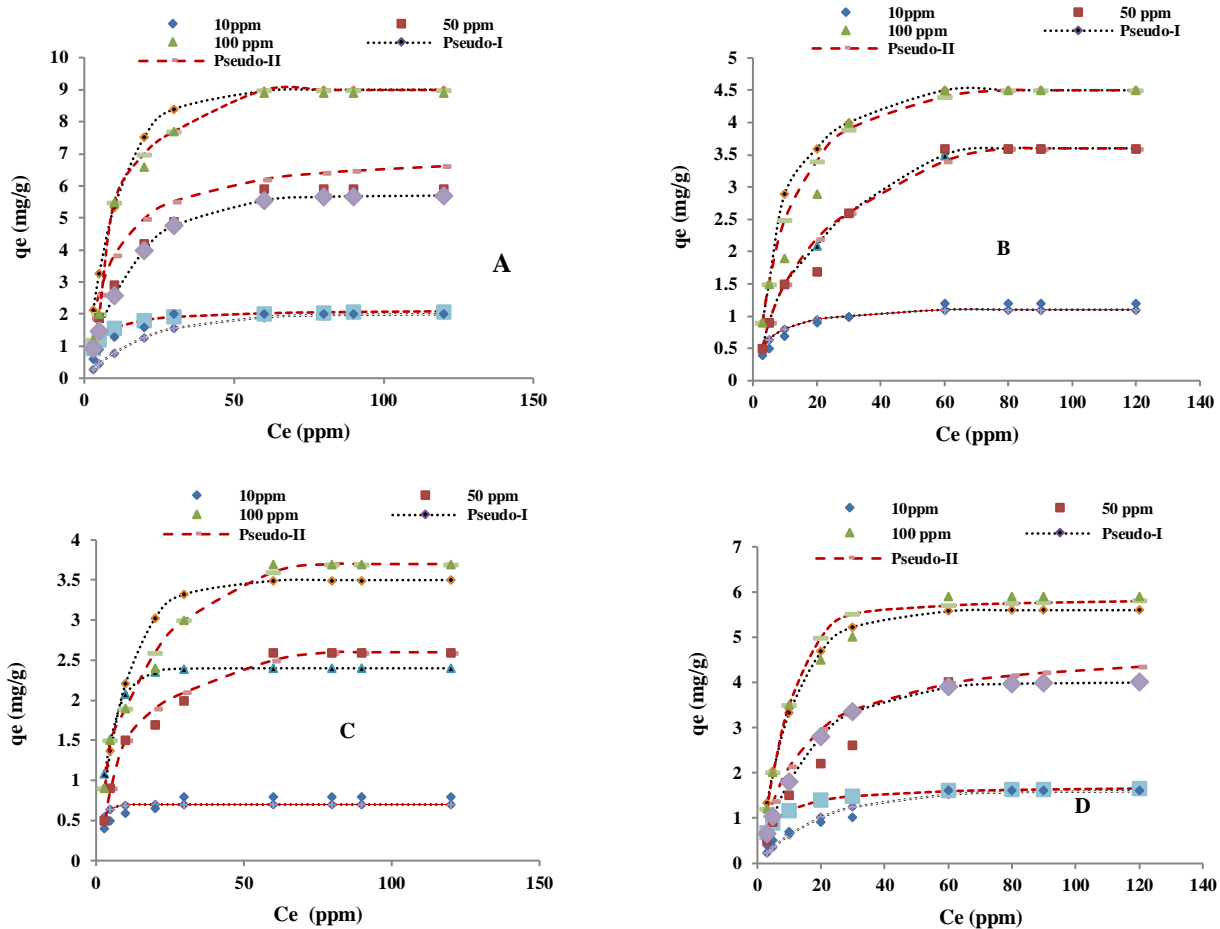


Fig.5: Biosorption kinetic models of A: MC-Pb (II), B: MC-Pb-Zn (II), C: MC-Cu (II), and D: MC- Cr (VI) ions by *Momordica Charantia*.

elucidate that the biosorption rate is reduced, and saturation in the micro-pores is augmented until equilibrium is achieved; this can be ascribed to a difference in the proportion of linking interactions. All experiment's max- biosorption-capacities were very near to the model. The increase in C_0 results in a reduction in the rate constant of PSO (k_2); a further reduction was shown as concentration further augmented. Moreover, this further indicates the relationship of the number of active sites and the rate of bio-adsorption since the accessibility of place is due to the initial concentration (C_0) and the time (t) at which equilibrium is attained [8].

Adsorption isotherms

Langmuir, Freundlich, and Timken isotherm model used to fit the equilibrium data obtained of the heavy

metals removal. These mathematical isotherm models are mainly employed for different adsorbent/adsorbate systems. Based on the theory of Langmuir isotherm, the adsorption process between adsorbent surface and adsorbate molecule is limited to monolayer with definite and localized active site; only a once site of adsorbate on the macromolecules are adsorbed. This empirical isotherm proposes that the adsorbent surface is homogenous and the energy of adsorption is identical for all adsorbent sites, and there is no link between adsorbed molecules [21]. On the other hand, the Freundlich adsorption model supposes that the adsorbent surface is a heterogeneous layer with several levels of adsorption temperatures and different affinity levels [20, 22]. The Timken model considers that the adsorption energy reduces linearly with the surface coverage owing to adsorbent/adsorbate links [7].

Non-linear equations of isotherm models employed are described as [2, 23, and 24]:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (5)$$

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (6)$$

$$q_e = K_F C_e^{\left(\frac{1}{n_F}\right)} \quad (7)$$

$$q_e = \frac{RT}{b_T} \ln A_T C_e \quad (8)$$

Where C_e is the concentration of each metal at equilibrium (ppm), q_e and q_{\max} (mg/g) are equilibrium and the maximum adsorption capacity, respectively, K_L (L/mg) is the Langmuir isotherm constant, R_L is the separation (dimensionless) factor, K_F is (mg/g)(L/mg)^{1/n} adsorption capacity, (1/n) is adsorption intensity, A_T (L/g) is equilibrium binding constant. b_T (kJ/mol) is adsorption energy. R (J/mol. K) is ideal gas constant. T (K) is temperature. Equilibrium data were studied under optimum conditions determined from the isotherm model predicted by Langmuir, Freundlich, and Temkin. The parameters of each model and the coefficient of correlation (R^2) are presented in Table 2. Isotherm model plots for sequestration of metal ions are shown in Fig.4. According to Fig.6 and Table 2, the equilibrium data are modeled better by the Langmuir isotherm compared to other models for all metal studied with high R^2 (0.998, 0.999, 0.997 and 0.998 for lead (II), Zinc (II), Copper (II), and Chromium (VI) ions, respectively). This result elucidates that the adsorption phenomenon proceeds as a monolayer on uniform surfaces. The maximum biosorption capacities are 8.9, 4.67, 3.9, and 5.91 mg/g for lead (II), Zinc (II), Copper (II), and Chromium (VI) ions, respectively. The values of K_L which are ascribed to the binding energy of the active site of MC are 0.05, 0.09, 0.05 and 0.06 L/g for lead (II), Zinc (II), Copper (II), and Chromium (VI) ions, respectively. The value of R_L vs initial metal ions concentrations between 10-120 mg/L are 0.66-0.14, 0.52- 0.08, 0.66-0.14, and 0.625-0.12 for Lead (II), Zinc (II), Copper (II), and Chromium (VI) ions, respectively. These results confirm that the bioprocess is favorable and reversible, owing to the R_L values ($0 < R_L < 1$) [17]. Additionally, it was observed that the variation of adsorption energy ($b_T < 8$) in the Temkin model, which validates the physical adsorption, was 2.4, 2.8, 2.98, and 2.71 kJ/mol for lead (II),

Zinc (II), Copper (II), and Chromium (VI) ions, respectively [25].

Thermodynamic study

To determine the impact of temperature on the removal of lead (II), Zinc (II), Copper (II), and Chromium (VI) ions onto MC, the bioprocess was affected at five temperatures between 298 to 333 K with 100 ppm of metal concentrations at pH=2 for chromium and pH=5 for other metals. The equilibrium metals ions capacities of the MC were higher at lower temperatures as the biosorption capacity of metal ions reduced with the increase in temperature. Thus, the bioprocess is not function at high temperatures [2]. Since biosorption processes are exothermic, the reduce in adsorbed uptake between 298 and 333K could be due to the harm of active sites in the Momordica Charantia. Temperature dependence of the bioprocess is related to three thermodynamic factors, including enthalpy (ΔH°), entropy (ΔS°), and free energy change (ΔG°), which are employed to define whether the bioprocesses are spontaneous or not. These parameters can be determined from the following formula [26, 28]:

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

$$K_c = \frac{a_s}{a_e} = \frac{Y_s}{Y_e} = \frac{C_s}{C_e} \quad (12)$$

Where K_c is the distribution factor, a_s is activity of adsorbed lead (II), Zinc (II), Copper (II), and Chromium (VI) ions, a_e is activity of heavy metal ions at equilibrium, Y_s is activity coefficient of lead (II), Zinc (II), Copper (II), and Chromium (VI) ions ions, Y_e is activity coefficient of lead (II), Zinc (II), Copper (II), and Chromium (VI) ions in equilibrium solution, C_s is lead (II), Zinc (II), Copper (II), and Chromium (VI) ions adsorbed on MC (mg/g), and C_e is heavy metal ions concentration at equilibrium (ppm). R is the universal gas constant (8.314 J/mol K) and T is the temperature in Kelvin. The results are shown in Table 1 The negative values of (ΔH°) articulate that the bioprocesses of all metals studied are exothermic in nature [9]. On the other hand, the values of (ΔH°) elucidate that linking of the heavy metal molecules to the Momordica Charantia is physical type [23]. Furthermore, the relative

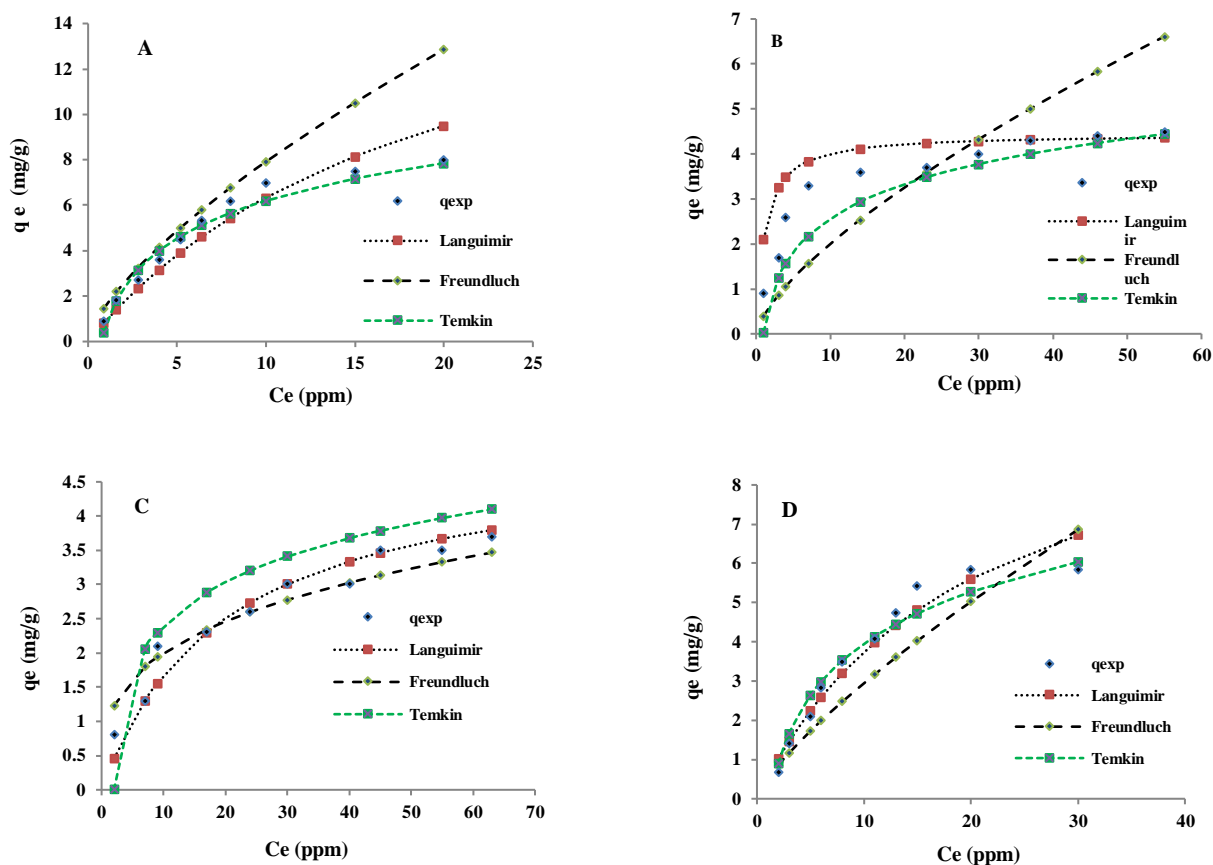


Fig. 6: Adsorption isotherm models of Pb, Zn, Cu and Cr ions by *Momordica Charantia*.

value of (ΔS°) indicates the high affinity between *Momordica Charantia* and heavy metal ions, and reflects the increment of the "disorder" parameter at the level of the biosorbent. Also, the negative values of (ΔG°) elucidate that all the bioprocesses studied are spontaneous [2, 29].

Desorption study

Cost-effectiveness is a significant parameter for the industrial practicability of bio-adsorbent. *Momordica Charantia* contains several site actives such as oxygen methylene, hydroxyl, and carboxyl, which can act as aligand or donor electron in the bio-adsorption [30]. Thus competition of organic sites can decrease the capacity of *Momordica Charantia* powder to adsorbed metal ions. The metal ion bind to *Momordica Charantia* can be studied by desorption technique after adsorption using *Momordica Charantia* at the reaction time and concentration of metal ion as shown in Fig.7. Several desorbing solutions such

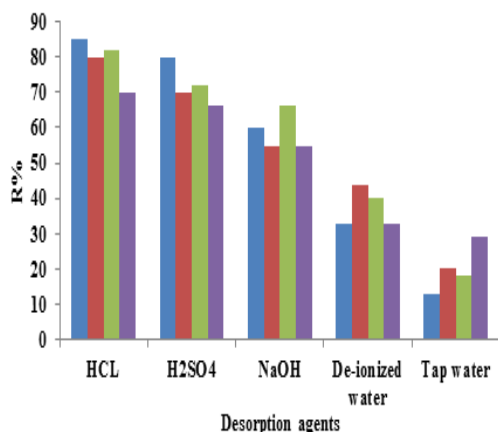
as 0.1 M NaOH, 0.1 M HCl, 0.1 M H_2SO_4 , tap water, and de-ionized water can be used systematically to desorbed metal ions from *Momordica Charantia*. Results show that HCl (0.1 N) is a powerful eluting solution than the rest, as seen in Fig. 7 for all metals studied. These results can be accepted due to several active sites involved in the bio-adsorption. For more specifications, the reproducibility of *Momordica Charantia* fibers was examined by applying three successive cycles of adsorption/desorption at optimum conditions. The results showed that bio-removal efficiencies were decreased from 8.2 to 4.3, 4.67 to 2.35, 3.9 to 1.13, and 5.4 to 2.01 mg/g for Pb (II), Zn (II), Cu (II), and Cr (VI), respectively. Thus, it can be concluded that the *Momordica Charantia* is good practical application in industrial purpose.

CONCLUSIONS

The present research demonstrated the capacity of lignocellulosic biomass *Momordica Charantia* for the

Table 1: Thermodynamic factors of lead (II), Zinc (II), Copper (II), and Chromium (VI) ions removal from aqueous solution by MC.

Metal ions	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	ΔG° (kJ/mol)				
			298K	303K	313K	323K	333K
Pb (II)	-5.8	-0.016	-1.032	-0.952	-0.792	-0.632	-0.472
Zn (II)	-7.11	-0.014	-2.93	-2.868	-2.728	-2.588	-2.448
Cu (II)	-10.77	-0.025	-3.32	-3.195	-2.945	-2.69	-2.450
Cr (VI)	-20.29	-0.05	-4.39	-5.140	-4.64	-4.14	-3.64

**Fig. 7: Desorption of Pb (II), Zn (II), Cu (II) and Cr (VI) ions adsorbed on Momordica Charantia.**

biosorption of lead (II), Zinc (II), Copper (II), and Chromium (VI) ions from an aqueous medium. *Momordica Charantia* was able to eliminate all the metals tested from solution, though with different removal efficiencies: lead > Chromium > Zinc > Copper. The thermodynamic factors such as enthalpy (ΔH°), entropy (ΔS°), and free energy change (ΔG°) biosorption confirm that the systems are spontaneous and exothermic. The equilibrium data have been modeled and fitted using Langmuir, Freundlich and Timken isotherm. The constants for each isotherm model and the coefficients of determination elucidate that the Langmuir isotherm was revealed to provide the goodness fit for all metal studied onto MC. The maximum sorption capacities are 8.9, 4.67, 3.9 and 5.91 mg/g for lead (II), Zinc (II), Copper (II), and Chromium (VI) ions, respectively. The kinetic study provided the high correlation of all metals' bio-adsorption equilibrium data onto MC by pseudo-second-order model. It can be conclude that since the *Momordica Charantia* is an easy and low-cost biosorbent and has a good

performance biosorption capacities, it can be treated as an alternative adsorbent for the treatment of heavy metals.

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